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Domain growth in Polyvinylidene Fluoride considered in terms of Ehrenfest transitions and nucleation theory

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A formalism is developed for predicting the critical nucleus size r_c and the critical free energy barrier ΔG_c for an isothermal polarization reversal. This is accomplished through the expansion of the excess free energy per unit volume, $g = (G_\beta - G_\alpha)/v_\beta$, of the transformed nucleus in a Maclaurin series in the electric field and then combining the result with classical nucleation theory to yield expressions for r_c and ΔG_c , which are then evaluated as functions of the interfacial energy γ for the case of 180° polarization reversal in β -polyvinylidene fluoride (β - PVF₂) using literature values for the parameters. The polarization domains are viewed as separate phases within the β -type crystals. An Arrhenius relationship is then used to independently calculate ΔG from polarization switching time data for the same system. These two sets of results are compared to obtain an estimate of the effective interfacial energy γ

for an assumed spherical nucleus. It is found that in the range of electric fields from 80 to 200 MV/m the value of γ is in the range of 20 to 40 mJ/m² and that γ decreases with decreasing electric field. The interfacial energy represented by γ is not the usual surface energy associated with polymer crystals. The point is made that γ need not be completely reversible in the sense of equilibrium thermodynamics but may have a dissipational component which is thought to be related to the polarization hysteresis loop.

I. INTRODUCTION

Polyvinylidene fluoride (PVF₂) is a semicrystalline polymer which has been extensively investigated in regard to its ferroelectric nature.¹⁻¹⁰ It is known that PVF₂ has a number of polar and non-polar phases.^{11-12,16,17} The polar β -phase is of special interest in this paper. It can be formed by uniaxial drawing of melt crystallized, non-polar α -PVF₂. Drawing transforms the TGTG' conformation of the α -phase to the planar zig-zag or all trans conformation of the β -phase. In this conformation the dipoles are aligned perpendicular to the chain axis (c-axis) and thereby give rise to the net polarization of the β -phase. To conform to the notation of our previous paper¹³ the symbols α and β in Section II below are used in a rather general sense and do not uniquely refer to the α and β phases as they are understood to apply specifically to PVF₂.

In this paper, classical nucleation theory is applied to a simplified model of 180° polarization reversal in β -PVF₂ in an electric field. The theory is developed with the assumption that a 180° rotation of the dipoles occurs in a localized volume which will be treated as a spherical nucleus of

reversed dipoles (Fig. 1). The domains of differently arranged dipoles will be viewed as separate phases (e.g., α and β in the notation of Section II). Work is in progress in which the nucleus is more realistically taken to be of a prismatic or cylindrical shape which encloses portions of one or more chain axes. In the present approximation, expressions are derived for the critical nucleus size r_c and the critical energy barrier ΔG_c required for a stable nucleus of reversed polarization to occur. These expressions are obtained by expanding the free energy in a Maclaurin series in the local electric field and incorporating these results with classical nucleation theory.

The paper is organized in the following manner. A brief background description of classical nucleation theory is given, beginning with Figs. 2 and 3 which clarify certain features of our notation, followed by the details of the free energy expansion and the development of expressions for r_c and ΔG_c . Literature values are used to compute r_c and ΔG_c vs. E and γ . This γ should not be confused with the usual interfacial energy for actual crystal growth in the polymer. It represents the effective interfacial energy of disaligned dipoles at the domain boundary. A separate estimation of the free energy barrier vs. E is computed using the data of Furukawa, Date, and Johnson³ and the two sets of ΔG_c values are compared and discussed in terms of future research directions.

II. RELEVANT ASPECTS OF NUCLEATION THEORY

A. The thermodynamic basis of nucleation in undercooled systems

The major fact underlying the need for a theory of nucleation is that a pure substance can exist for substantial, sometimes indefinite, periods of

time in an undercooled condition. For example very pure water can remain in the liquid phase at a temperature as low as -40°C (at 1 atmosphere). If an equilibrium phase α exists for a given set of intensive variables (T_1, p_1, E_1, \dots) and if equilibrium thermodynamics predicts that a new equilibrium phase β should exist for a new set of intensive variables (T_2, p_2, E_2, \dots), it is the usual situation that the expected transformation

$$\alpha \rightarrow \beta \quad (1)$$

will not occur instantaneously, and in fact may be very slow. The reason for this inhibition of the expected transformation is that even when local density fluctuations and diffusive motions lead to the formation of a small nucleus of β -phase (see Section I) within the α -matrix, the energy $\gamma_{\beta}A_{\beta}$ associated with the interface A_{β} increases the total Gibbs' free energy and thus opposes the formation of the β -phase; which if formed in bulk would be stable. The total Gibbs energy corresponding to a growing nucleus of volume V_{β} can be written as

$$\Delta G = gV_{\beta} + g_s V_{\beta} + \gamma_{\beta} A_{\beta} \quad (2)$$

where an excess free energy density of the β -phase is given by

$$g = (G_{\beta} - G_{\alpha})/v_{\beta} \quad (3)$$

and g_s is an effective strain energy density which will not be explicitly treated in the present work. The ordinary (bulk) molar free energies and molar volume are denoted by G_{α} , G_{β} and v_{β} , respectively.

As discussed previously (BCI)¹³, the size of the critical nucleus r_c , corresponds to the maximum (ΔG_c) of the free energy surface. Thus, for a spherical nucleus

$$r_c = -2\gamma/g \quad (4)$$

and

$$\Delta G_c = (16\pi/3)\gamma^3/g^2. \quad (5)$$

For generality it can be assumed that both γ and g depend on the temperature T and other intensive variables as well, such as pressure p and electric field intensity E . Our postulate is that γ need not be strictly analogous to an ideal equilibrium interfacial free energy, as in classical thermodynamics, but may have a partially irreversible character, as in fracture with craze formation. This assumption opens the possibility of associating polarization hysteresis loops to the irreversible (dissipational) component of γ . In the usual case treated in nucleation theory, viz. the case of $p = 0.1$ MPa and $E = 0$, one is concerned with the degree of undercooling, $\theta = (T_t - T)$, and, as shown previously¹³

$$r_c = -[2\gamma(T_t/\theta) h_t^{-1}] [1 - \eta\theta + \dots]^{-1} \quad (6)$$

$$\Delta G_c = [(16\pi/3)\gamma^3(T_t/\theta)^2 h_t^{-2}] [1 - \eta^2\theta^2 + \dots]^{-1} \quad (7)$$

where

$$\eta \equiv (\Delta C_p/2v_\beta h_t) - \alpha_\beta \quad (8)$$

and the symbols h_t , C_p , and α_β denote the excess enthalpy density $(H_\beta - H_\alpha)/v_\beta$, the heat capacity, and the volumetric thermal expansivity.

B. Thermodynamic analysis for the effect of an electric field

In the previous section, simple expressions for the critical nucleus size and critical energy barrier are described which depend only on γ the effective interfacial energy of the polarization domain and g the excess free energy per unit volume of the transformed polarization nucleus. In this section a method of evaluating g will be described for the case of an applied electric field in an analogous manner to the method of Barker and Campbell¹³ for the case of supercooling at constant pressure and field strength.

1. Free energy as a Maclaurin series in electric field strength

It is possible to construct a useful formalism by expanding the effective free energy of the transformed nucleus g in a Maclaurin series in E (the local electric field) and then, using thermodynamical relations, to evaluate the expansion coefficients. For example if

$$g = g(E) = g(0) + g'(0)E + \frac{1}{2}g''(0)E^2 + \dots \quad (9)$$

$$= a_0 + a_1E + a_2E^2 + \dots \quad (10)$$

then $g'(0)$, which means $\partial g / \partial E)_T$ at $E = 0$, can be found as follows:

Let D_α and D_β represent the electric displacements (with an implicit tensor character) and define a Gibbs free energy difference as

$$G_\beta - G_\alpha = H_\beta - H_\alpha - T(S_\beta - S_\alpha) - (v_\beta ED_\beta - v_\alpha ED_\alpha) \quad (11)$$

so that, upon using Eq. (3), one can obtain

$$\left(\frac{\partial g}{\partial E} \right)_T = \frac{1}{v_\beta} \left[\left(\frac{\partial G_\beta}{\partial E} \right)_T - \left(\frac{\partial G_\alpha}{\partial E} \right)_T \right] \quad (12)$$

and therefore

$$g'(0) = (v_\alpha / v_\beta) D_\alpha - D_\beta \quad (13)$$

Note that $g(0)$ is zero by definition of the equilibrium transition.

Similarly

$$g''(0) = \left(\frac{\partial^2 g}{\partial E^2} \right)_T \Big|_{E=0} = \frac{\partial [(v_\alpha / v_\beta) D_\alpha]}{\partial E} - \frac{\partial D_\beta}{\partial E} \Big|_{E=0} \quad (14)$$

which yields

$$g''(0) = \frac{v_\alpha}{v_\beta} \frac{\partial D_\alpha}{\partial E} + \frac{D_\alpha}{v_\beta} \frac{\partial v_\alpha}{\partial E} - \frac{v_\alpha}{v_\beta^2} \frac{\partial v_\beta}{\partial E} D_\alpha - \frac{\partial D_\beta}{\partial E} - \frac{v_\alpha}{v_\beta} \frac{\partial v_\beta}{\partial E} D_\alpha + \frac{D_\beta}{v_\beta} \frac{\partial v_\beta}{\partial E} \quad (15)$$

However if $(\partial v_\alpha / \partial E)_T$ and $(\partial v_\beta / \partial E)_T$ are negligible, then

$$g''(0) = (v_\alpha / v_\beta) \epsilon_\alpha - \epsilon_\beta \quad (16)$$

where ϵ_α is the permittivity, $\kappa_\beta \epsilon_0$.

The preceeding equations reveal that

$$\begin{aligned} a_0 &= 0, \quad a_1 = (v_\alpha / v_\beta) D_\alpha - D_\beta \\ a_2 &= [(v_\alpha / v_\beta) \epsilon_\alpha - \epsilon_\beta] / 2 \end{aligned} \quad (17)$$

These results when substituted into Eq. (9), yield the following expression for $g(E)$

$$g(E) = [(v_\alpha / v_\beta) D_\alpha - D_\beta] E + (\frac{1}{2}) [(v_\alpha / v_\beta) \epsilon_\alpha - \epsilon_\beta] E^2 + \dots \quad (18)$$

2. Expressions for r_c and ΔG_c

The expansion for g can be substituted into Eqs. (4) and (5) to provide expressions for the critical nucleus size and critical energy barrier for an isothermal transition influenced by an electric field giving

$$r_c = - \frac{2\gamma}{[(v_\alpha / v_\beta) D_\alpha - D_\beta] E + (\frac{1}{2}) [(v_\alpha / v_\beta) \epsilon_\alpha - \epsilon_\beta] E^2} \quad (19)$$

$$\Delta G_c = \frac{(16\pi/3)\gamma^3}{\{[(v_\alpha / v_\beta) D_\alpha - D_\beta] E + (\frac{1}{2}) [(v_\alpha / v_\beta) \epsilon_\alpha - \epsilon_\beta] E^2\}^2} \quad (20)$$

The anisotropic character of the polymer is at least partially accounted for by using the appropriate components of the dielectric tensor. From BC-1 we infer that the expression for r_c when ordinary undercooling is also involved will contain the following extra terms in the denominator

$$(h_t / T_t) \theta - [(\Delta G_p / 2v_\beta T_t) - \alpha_\beta h_t / T_t] \theta^2 + \dots$$

and the critical barrier will have these same terms, added before squaring, in the denominator of Eq. (20). The field E is not the macroscopic external field E_0 but rather the local field which is experienced by the nucleus of reversed polarization. The local field is the field experienced by a

dielectric sphere embedded in a matrix with a different dielectric constant. Thus the relationship between the local electric field E in the above equations and the applied electric field E_0 is

$$E = \frac{3\varepsilon_\alpha}{2\varepsilon_\alpha + \varepsilon_\beta} E_0 \quad (21)$$

III. PREDICTIONS OF MAGNITUDES FOR PVF₂

A. Estimates of r_c and ΔG_c from nucleation theory

Values for the unknown terms in Eqs. (19) and (20), the electric displacement and the permittivity, were taken to be equal in magnitude but opposite in direction for the polarization reversal. Thus, $D_\beta = -D_\alpha$ and $\varepsilon_\beta = -\varepsilon_\alpha$ where the positive direction is taken to be that of the electric field. Using literature values of $\pm 65 \text{ mC/m}^2$ for the electric displacement⁹ and $\pm 2.66 \times 10^{-11} \text{ F/m}$ for the permittivity², with the \pm relating to the β -phase and α -phase respectively, values were generated for r_c and ΔG_c . Results for the critical radius versus the electric field assuming $\theta = 0$ are shown in Fig. 4. Since the effective interfacial energy γ is unknown, it is taken as a parameter between 5 and 25 mJ/m^2 for the analysis. On an intuitive basis the results appear reasonable.

Similarly, the values of the free energy barrier ΔG_c are plotted against electric field in Fig. 5. Again γ is taken as a parameter. In this case the predicted free energy barrier for a given field strength changes by two orders of magnitude as γ changes from 5 to 25 mJ/m^2 . One should not be surprised if γ is field dependent since it corresponds to the misorientation energy of the dipoles near the domain boundary. However for high electric fields, above

about 100 MV/m, the value of Δ_c is less than 100 kJ/mol regardless of the choice of the interfacial energy up to the maximum value on the graph ($\gamma = 25$ mJ/m²).

B. Direct estimate of Δ from polarization switching data

Furukawa, Date, and Johnson³ have presented some very useful measurements of polarization switching times τ_s vs E and T. We have found that a reanalysis of their data as Arrhenius plots (Fig. 6) with E as a parameter exhibit fairly well defined linear regions of $\log \tau_s$ vs $1/T$ above 250 K. From such plots activation barriers can be determined, and they turn out to have a systematic field dependence. The activation energies, determined from these data are given in Fig. 7. Takose and Odajima¹⁸ also have briefly mentioned a "activation energy" of 0.63 eV (61 kJ/mol) at 200 MV/m for the characterization of the peaks of polarization switching curves. However, they do not develop the idea into the framework of a more detailed model as we are attempting here. Another interesting feature of the plots in Fig. 6 is that within the accuracy of the data all the curves appear to converge to a common intersection at $1/T \sim 2.5 \times 10^{-3} \text{ K}^{-1}$ and $\tau_s \sim 10^{-7} \text{ s}$. The apparent linearity of the relation between Δ_c and E suggests, rather plausibly, that the activation barrier is biased by the presence of the field, so that

$$\tau_s = \tau_s^0 \exp(\Delta / RT) \quad (22)$$

where

$$\Delta = \Delta_0 - m \cdot E \quad (23)$$

and m is an effective dipole moment of the cluster of dipoles which participate in a switching event. An extrapolation to $E = 0$ gives $\Delta_0 \approx 100 \text{ kJ/mol} \approx 1 \text{ eV/event}$ in the absence of the field, which does not appear unreasonable.

C. Comparison of the values found for the energy barrier

The motivation for constructing the Arrhenius plots as discussed above was to have an independent method of estimating ΔG_c to see if a reasonable correspondence between the values obtained by the two methods could be found. Then it would be possible to estimate the interfacial energy γ by allowing γ to have the value which would give the best agreement between the two calculations and the switching time data. The effect of any actual interfacial energy is only implicit in the value of ΔG_c obtained through the Arrhenius plot method. When the two sets of results are compared, it is seen that a reasonable correspondence between the orders of magnitude is achieved but that some of the detailed trends require discussion. When an estimation of the interfacial energy is attempted the value appears to lie in the 20 to 40 mJ/m² range for electric fields between 80 and 200 MV/m. However, the line obtained by plotting ΔG_c found via the Arrhenius method on the same graph as the nucleation theory method (Fig. 8) is not parallel to the lines drawn for constant interfacial energy. This suggests that the effective interfacial energy is a function of the electric field strength, as would be expected if the E field modifies the local interactions between dipoles as the chain conformations change.

D. Comments on reversible and irreversible aspects of polarization

Changes in polarization of PVF₂ involve irreversible processes corresponding to hysteresis loops of the type shown in Fig 8a, with an entropy production of $\int E \cdot dP/T$ per unit volume per cycle. therefore a proper account of polarization kinetics in this material should utilize non-equilibrium

thermodynamics. However in the present work we wish to employ a frame-work based mainly on an equilibrium thermodynamics. We have drawn heavily on our preceding paper (BC1)¹³ in which the applications of nucleation theory to Ehrenfest thermodynamic transitions were considered. An important generalization which we have realized in connection with the present paper, but which transcends it in breadth and importance, is that the interfacial energy term γ , which appears in nucleation theory does not have to be strictly thermodynamic (i.e., non-dissipational) in character. Thus when a general phase β is nucleated within a general phase α , the opposing interfacial energy term $\sum \gamma_{\beta\alpha} A_{\beta}$ can involve ductile work or other types of irreversible work. In the case of ferroelectric polymers we think that the more general type of interfacial energy can be associated with the hysteresis behavior of reorienting dipoles.

If it were not for the hysteresis, then the polarization would be reversible and very much easier to treat. It still seems useful to consider the simplest case of a reversible two state system with a saturation polarization $P_s = n\mu$, where for PVF₂, $\mu = 7.3 \times 10^{-30}$ C-m and n is the number density of dipoles.⁶ It is well known that such a two state paraelectric model has a polarization given by¹⁹

$$P = (n_+ - n_-)\mu / (n_+ + n_-) = P_s \tanh(aE) \quad (24)$$

where n_+ and n_- denote dipole concentrations with and against the field and $a = \mu/kT$. From thermodynamics, the polarization is given by

$$P = -V^{-1} (\partial G / \partial E)_T \quad (25)$$

so that, as an alternative to Eq. (9),

$$[G(E) - G(0)]_{T,V} = -V \int_0^E P \cdot dE. \quad (26)$$

Then, using the result for the two state model,

$$\begin{aligned} G(E) &= G(0) - P_s V \int_0^E \tanh(aE) dE \\ &= G(0) - (VP_s/a) \ln \cosh(aE) \end{aligned} \quad (27)$$

For small E this function is approximately parabolic and for large E it becomes linear. The general shape is illustrated schematically in Fig. 9a. For sudden field changes, $\Delta E = E_2 - E_1$, the thermodynamic "driving force" for the reorientation of dipoles is ΔG_{12} . If the field is suddenly reversed, the ΔG between the curve and its mirror image would be the driving force. When hysteresis is present, the situation is very much more complicated but one can try to draw certain parallels of free energy vs field for the actual polarization curve. Such schematic representations of the free energy are represented in Fig. 8b. We are grateful to A. S. DeReggi of NBS for the polarization hysteresis data of Fig. 8a.

IV. DISCUSSION AND CONCLUSIONS

A number of features of a simple model for the nucleation of polarized domains in ferroelectric polymers have been explored. The physical basis of the model is that dipole reorientation, even in the presence of a field going in the "wrong direction," will not occur unless fluctuations at a small microstructural level produce one or more "nuclei" of reoriented polarization of sufficiently large volume to overcome an effective interfacial energy barrier which can be viewed as partially reversible and partially dissipational. In PVF_2 the interfacial energy is presumed to be related to the production of Reneker defects or similar kinks in a zone surrounding the reoriented dipoles. The model here differs significantly from that of Drey-Aharon et al.⁵ in that their kink propagation mechanism involved the soliton like propagation of a rotational disturbance via an equation for the Hamiltonian containing rotational kinetic energies.

By applying the ideas of classical thermodynamic nucleation theory to the present model (assuming quasi-spherical nuclei) expressions for the size of the critical nucleus and the critical energy barrier were obtained. A limited accounting for anisotropy is included by using the appropriate components of the dielectric tensor. The approach is to expand the excess free energy per unit volume of transformed material as a Maclaurin series in the field intensity E , first assuming that the sample is at the equilibrium temperature for the transformation to occur. Equations (19) and (20) result from this technique and these are plotted in Figs. 4 and 5. It needs to be recognized that these expressions over-emphasise the influence of the field if the sample already is at some finite degree of undercooling. Thus, there may be much less difference in the slopes of the corrected ΔG vs E curves based on the nucleation theory and the ΔG vs E plots based on the polarization switching measurement of Furukawa, Data and Johnson.³ The numerical values for the plots of the parameters r_c and ΔG_c of nucleation theory were obtained from the literature for PVF_2 .^{2,9,14,15} If these plots are taken at face value, one must postulate a field dependent interfacial energy in order to bring the two approaches into agreement. Although, a field dependent γ seems quite plausible, and in the light of the discussion above even probable, it is felt that any true dependence will be weaker than an analysis of Fig. 5 would imply. This is because the actual nucleation will occur at a finite degree of undercooling θ . Even in the extreme case considered ($\theta = 0$), the values needed for the interfacial energy fall within the range 20 to 40 mJ/m² (increasing for fields between 80 and 200 MV/m) and seem to be of a physically reasonable magnitude. It amounts to about 1 kJ/mol of kinks.

There are many possible extensions and modifications that might be hoped to provide better models for the polarization switching process. Several are

now being considered, for example a more realistic shape for the nucleus such as a cylinder or prismatic volume parallel to the chain axis. Another major concern is that of finding a better way to account for the irreversibility (hysteresis of P vs E). A rotational "dry friction" model is being considered, along with the possibility of trying to incorporate Broadhurst's^{14,15} approach of writing the free energy as a sum of terms $G' = \sum G'_s$ over all rotational sites s for a collective dipole m where

$$G'_s = -V_0 f_s^2 - V_1 f_s \cos n\theta_s - mE f_s \cos\theta_s + kT f_s \ln f_s$$

and where f_s is the fraction of dipoles in site s , at orientation angle θ_s , and V_0 , V_1 are parameters with the dimensions of energy. The Broadhurst potential has the property that a spontaneous transition from a given metastable minimum is opposed not so much by the V_0 barrier for a dipole but by the low probability that a macroscopic region of the crystal will experience the needed cooperative energy fluctuation to allow the transformation.

The influence of very inhomogeneous electric fields and the effect of the non-crystalline ($\sim 50\%$) fraction of PVF_2 on the nucleation and growth processes are other concerns.

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FIGURE CAPTIONS

- Fig. 1. Schematic illustrating a model for the 180° polarization reversal in β -PVF₂ in which a spherical nucleus of reversed dipole orientation forms under the influence of an electric field.
- Fig. 2. For a phase transition $\alpha \rightarrow \beta$ to occur at a degree of supercooling θ , G_β must be less than G_α where G is the ordinary molar Gibbs' free energy. α and β are general designations for phases, not necessarily the α and β phases associated with PVF₂.
- Fig. 3. The two opposing energy terms which give rise to a critical radius r_c and a critical energy barrier ΔG_c for the stable existence of a nucleus. The proposed influence of an electric field on the two terms and on the critical values is illustrated schematically.
- Fig. 4. A plot of the critical nucleus radius r_c vs. the applied electric field for the case of 180° polarization reversal in β -PVF₂ as a function of the interfacial energy γ . Note that the saturation field of 210 MV/m corresponds to the molecular dimensions of the PVF₂-mer for $\gamma = 25 \text{ mJ/m}^2$.
- Fig. 5. A plot of the critical energy barrier ΔG_c vs. the applied electric field for the case of 180° polarization reversal in β -PVF₂ as a function of the interfacial energy γ . The data points pertain to Fig. 7.
- Fig. 6. A plot of the switching time τ_s vs. the inverse temperature for polarization reversal in β -PVF₂ using the data of Furukawa et al.³.
- Fig. 7. A plot of the activation energy ΔG_c vs. the applied electric field. the data were obtained through the use of an Arrhenius-type relationship using the experimental data of Furukawa et al.³.

Fig. 8a. Hysteresis loop for PVF_2 (DeReggi et al.).

Fig. 8b. Free energy curves obtained by modeling the P vs E behavior after the $\tanh(aE)$ relation of Fig. 9.

Fig. 9a. Schematic illustration of the $\tanh(\mu E/kT)$ polarization curve corresponding to a model consisting of non-interacting dipoles with two energy states ($+\mu E$ and $-\mu E$).

Fig. 9b. Free energy curves obtained by integrating the $\tanh(aE)$ curve. The dashed curve is for field reversal.

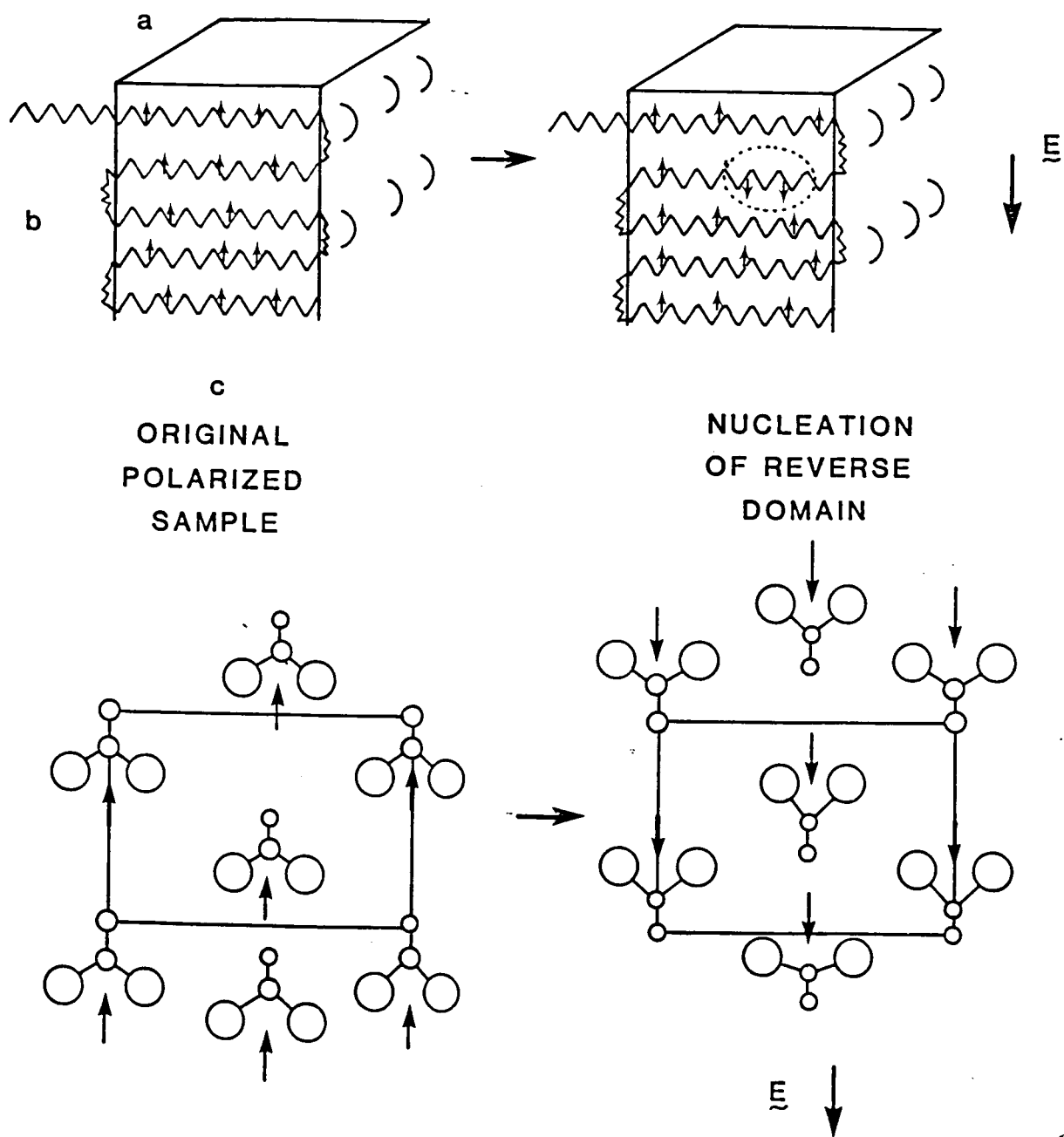


Figure 1

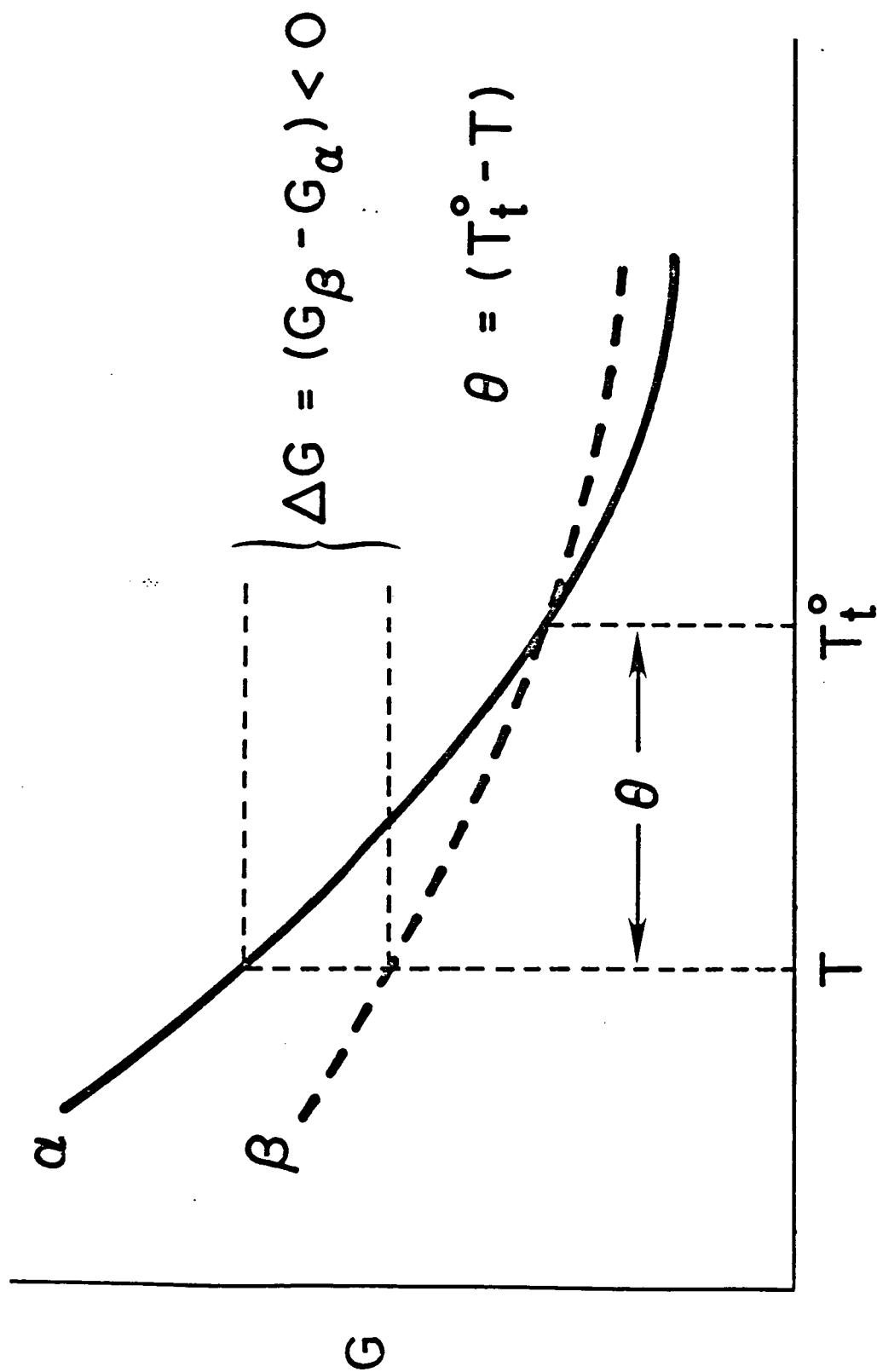


Figure 2

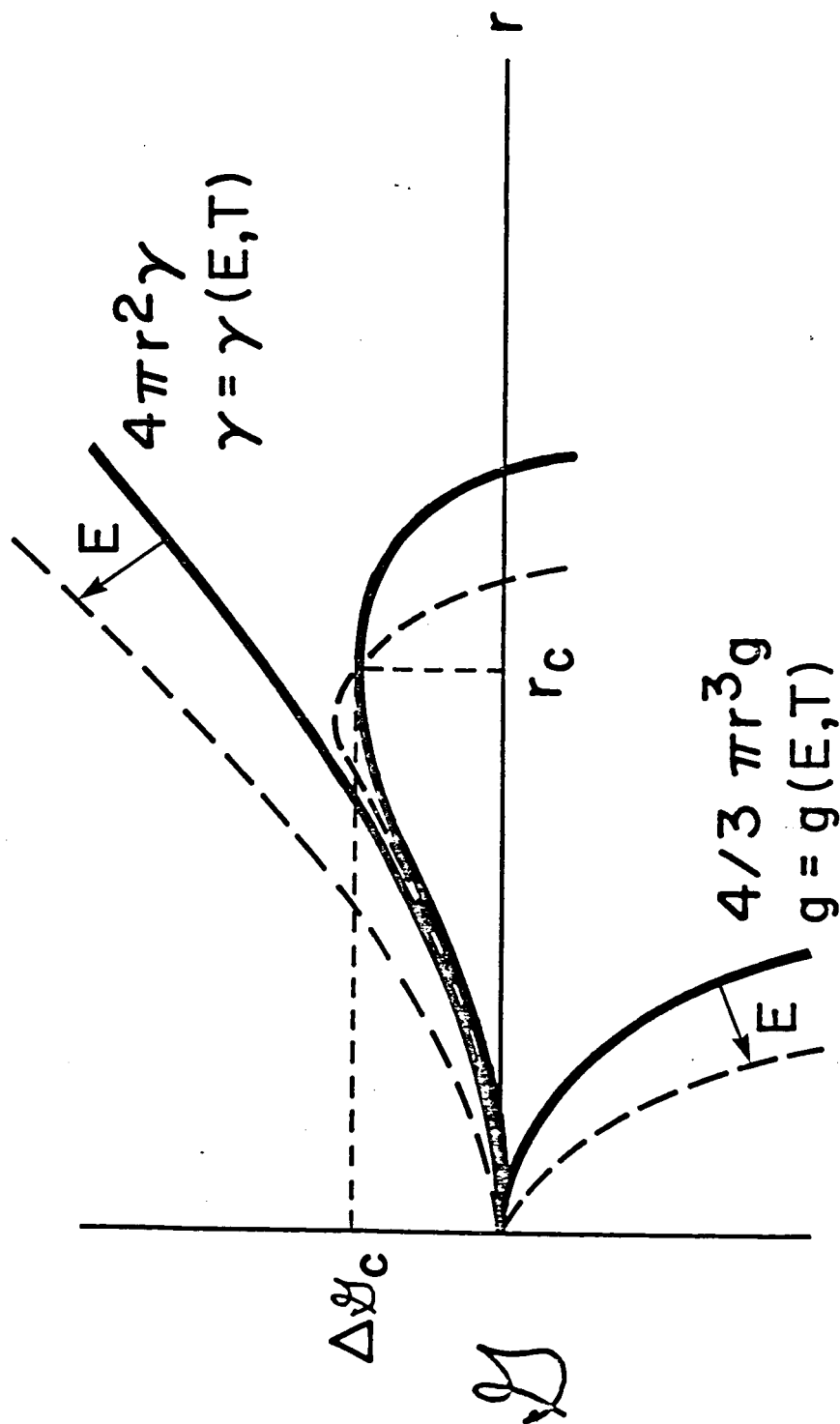


Figure 3

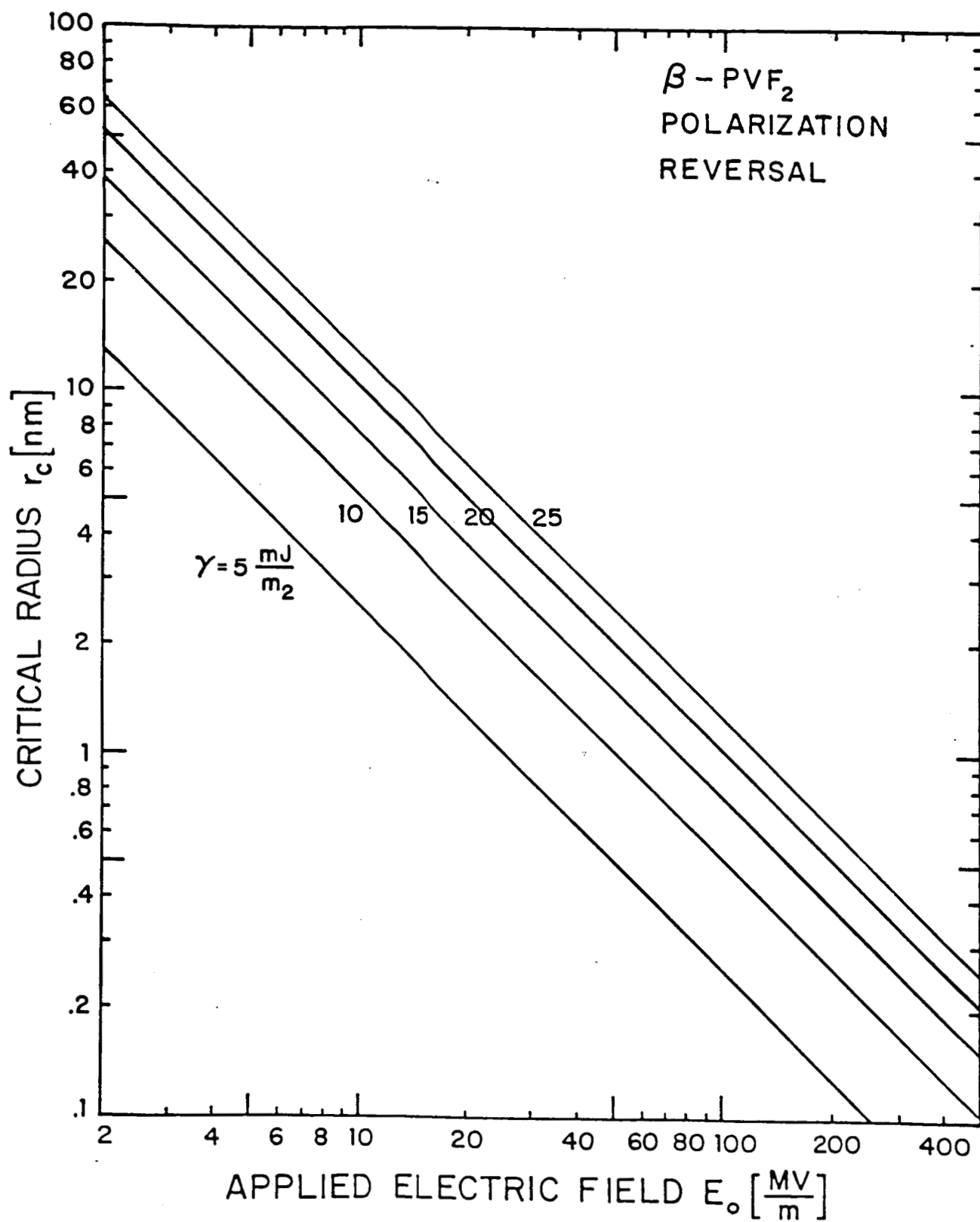


Figure 4

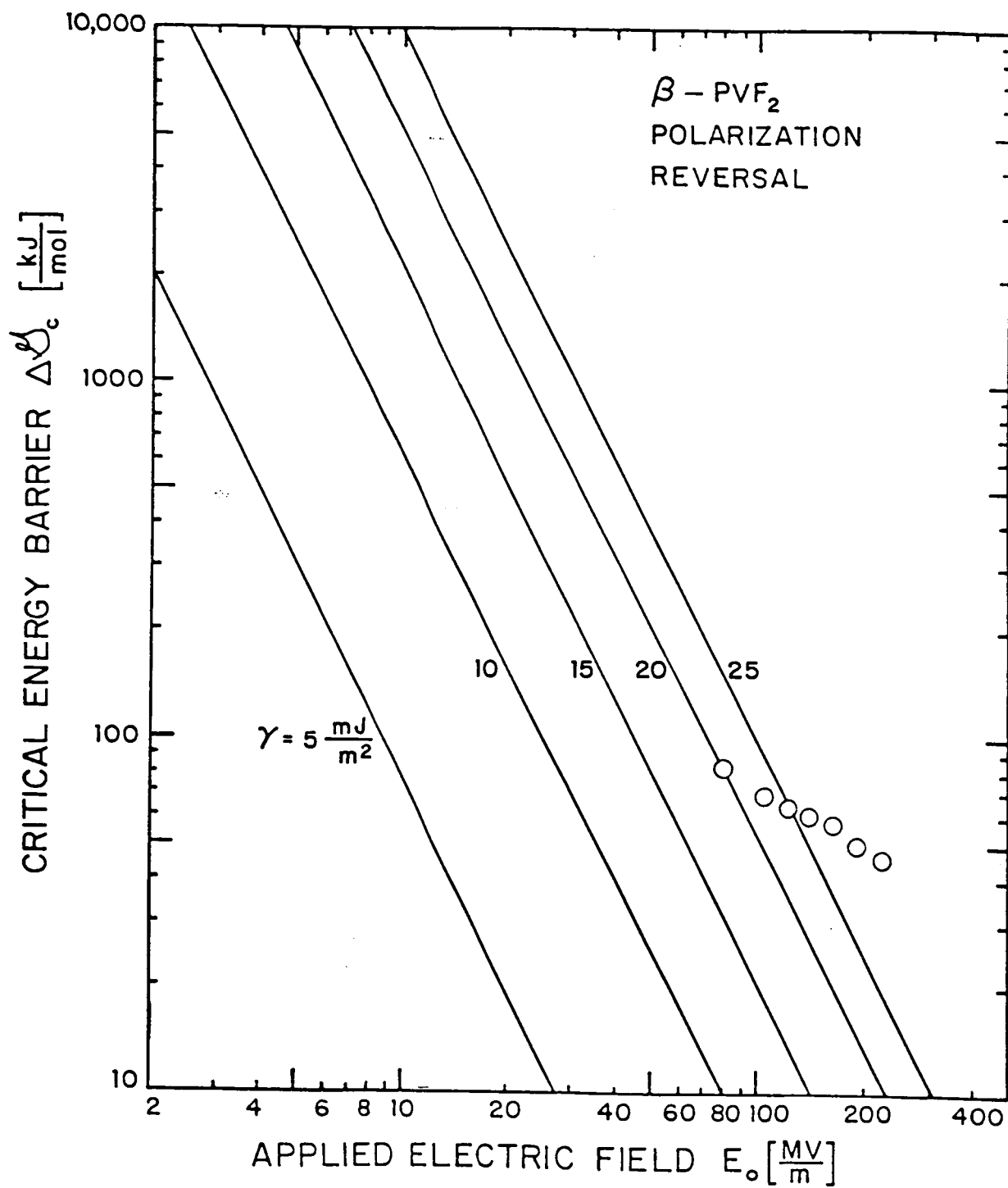


Figure 5

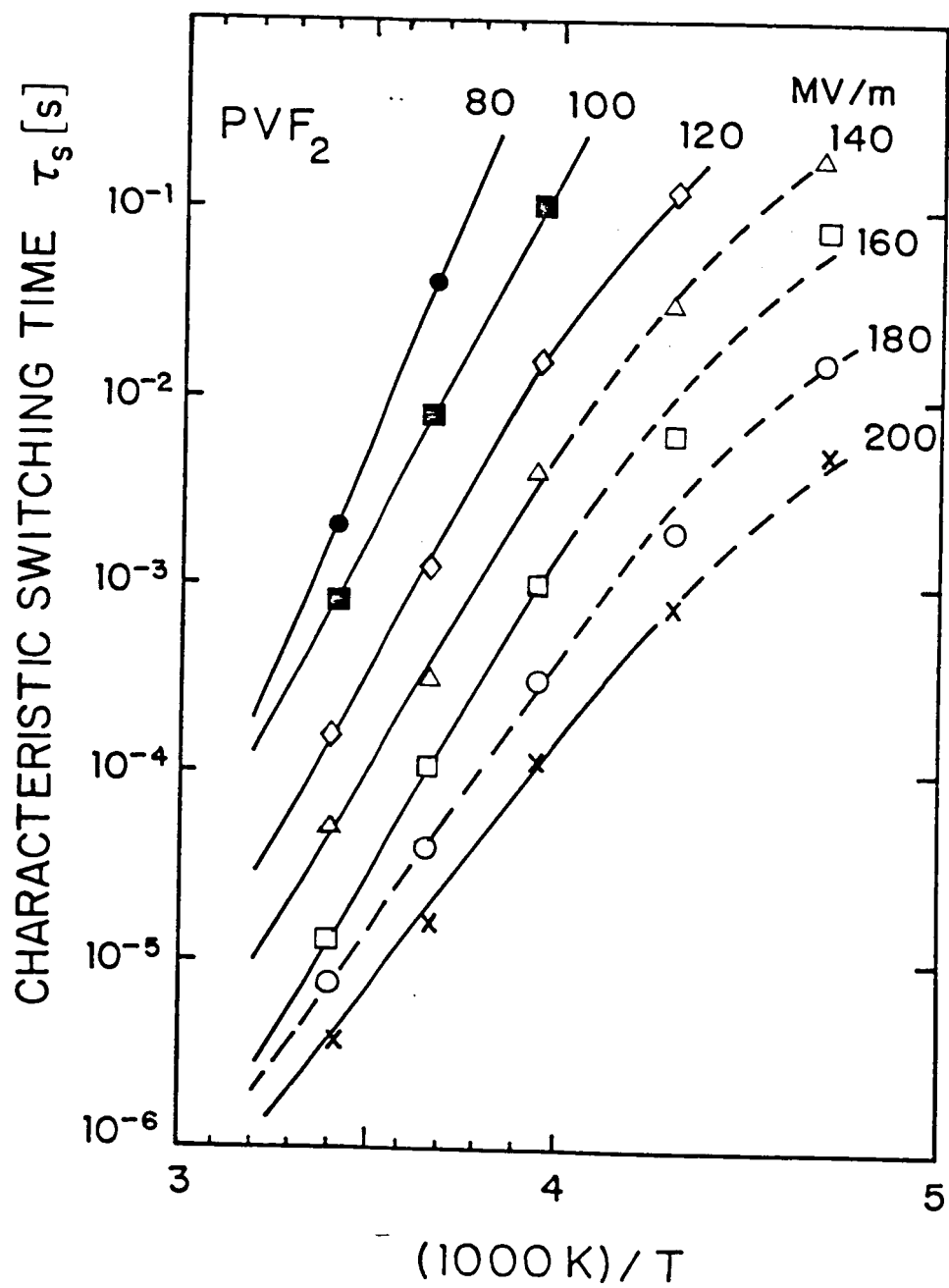


Figure 6

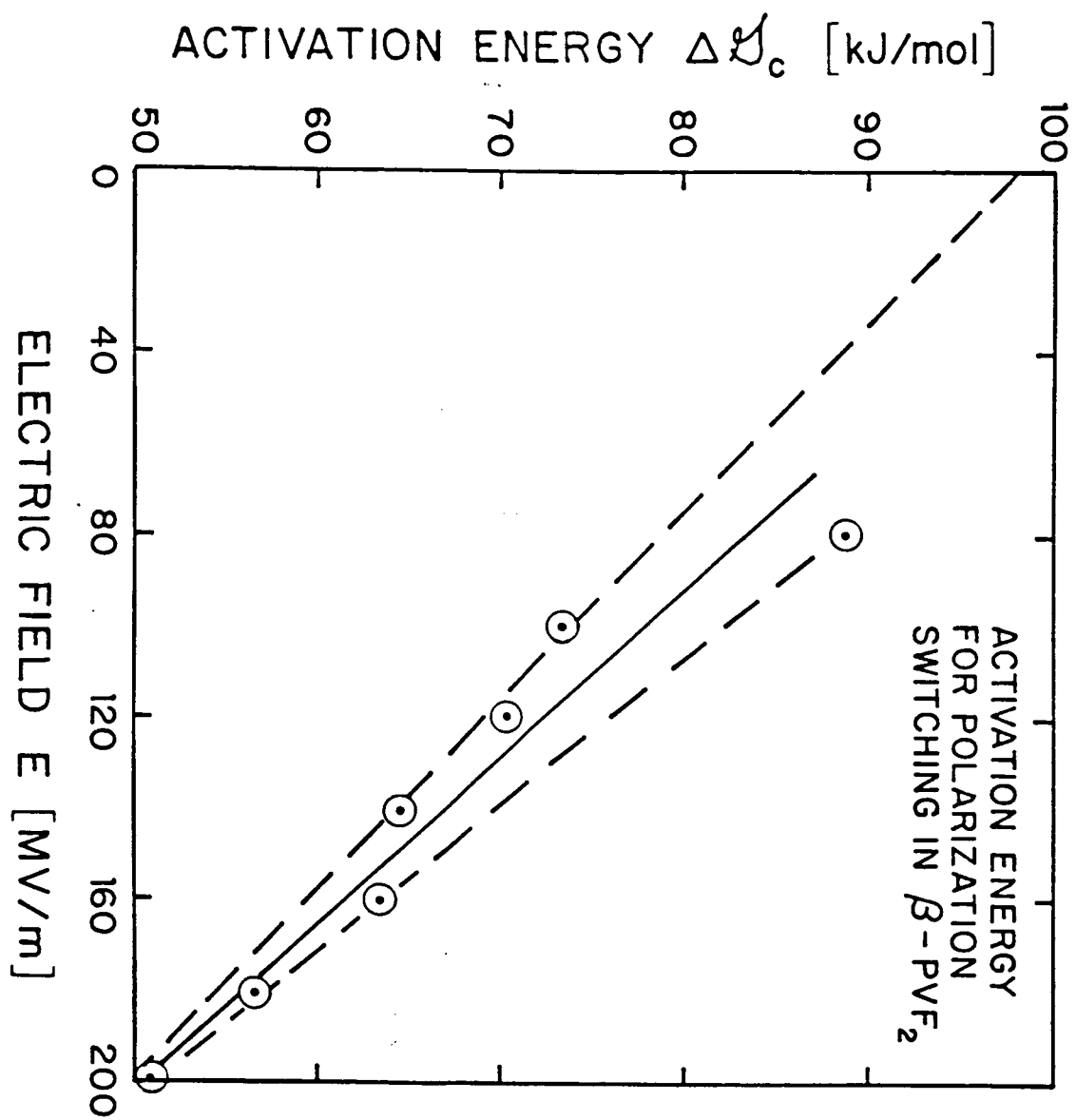
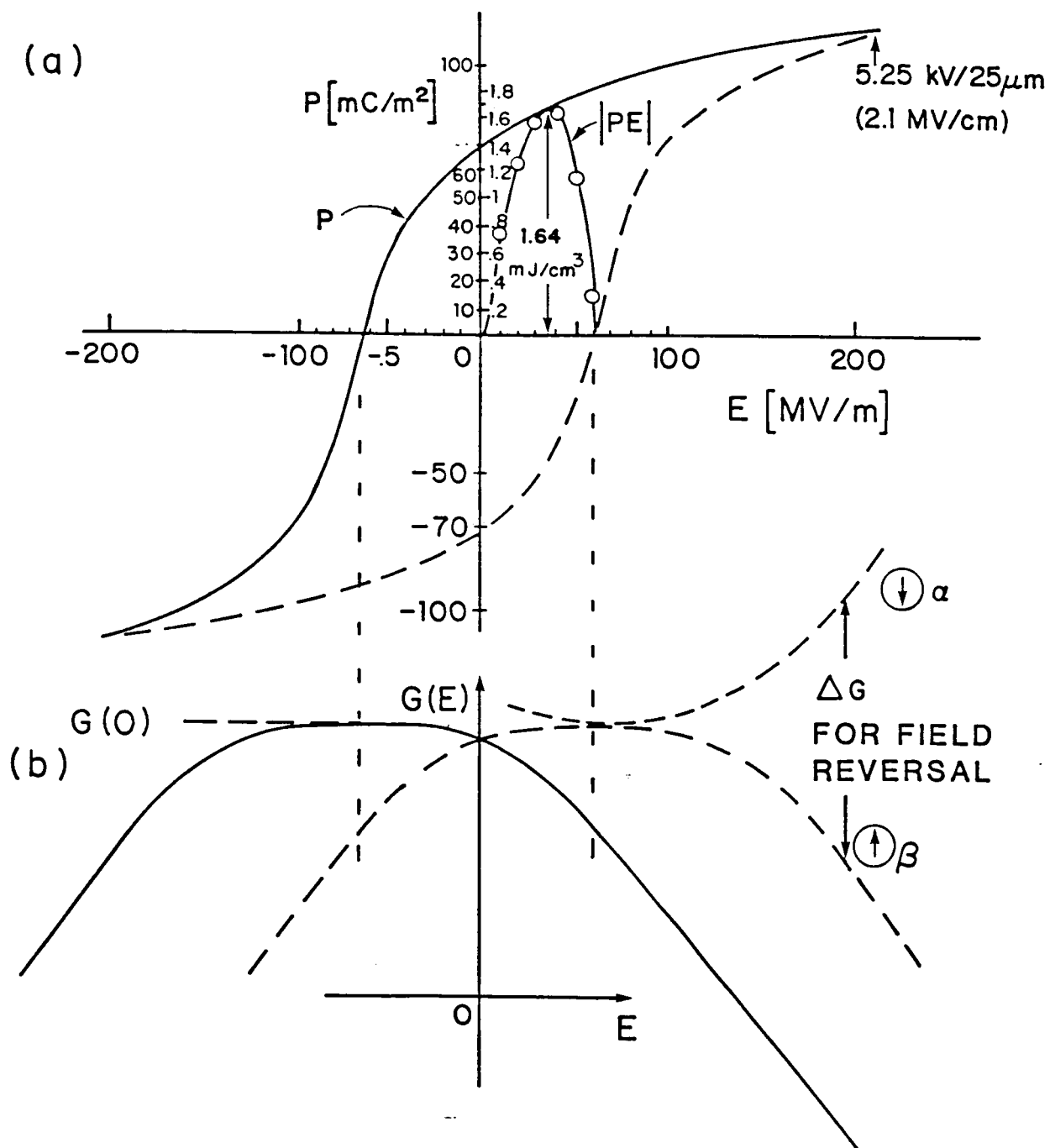
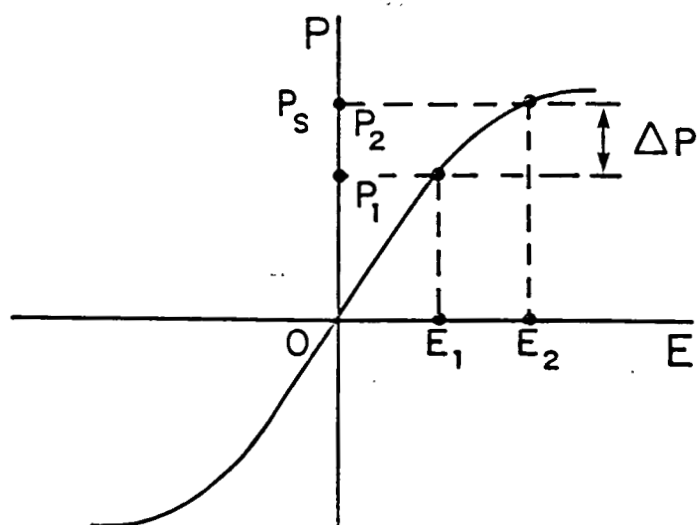


Figure 7

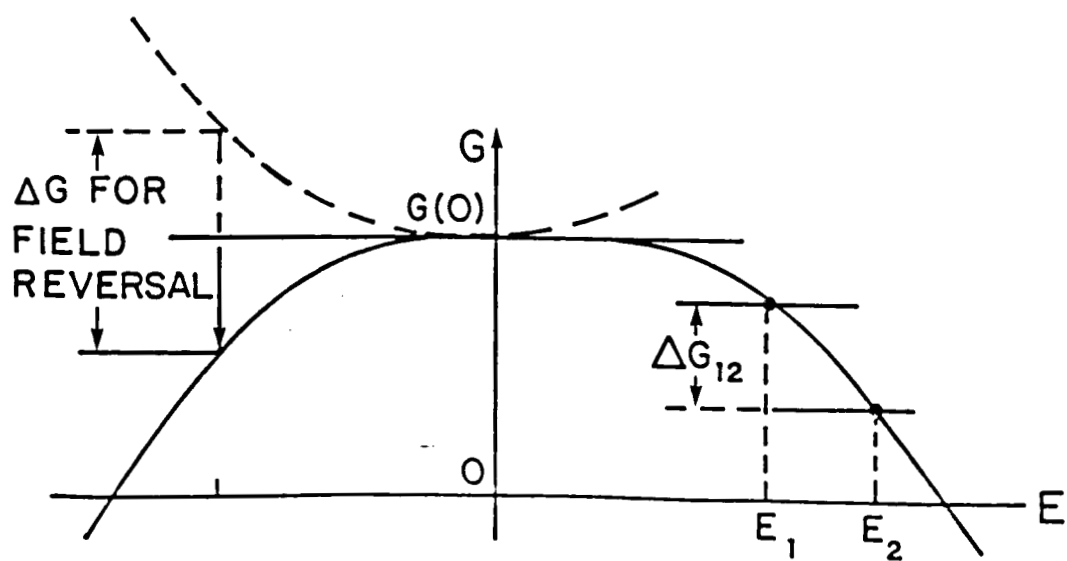


Figures 8a and 8b

(a)



(b)



Figures 9a and 9b